Spiropyran-terthiophene Polymers as Multi-Stimuli-Responsive Platforms for Biochemical Interactions

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"Considerate la vostra semenza: fatti non foste per viver come bruti, ma per seguir virtute e canoscenza".

"Consider well the seed that gave you birth: you were not made to live your lives as brutes, but to be followers of worth and knowledge".

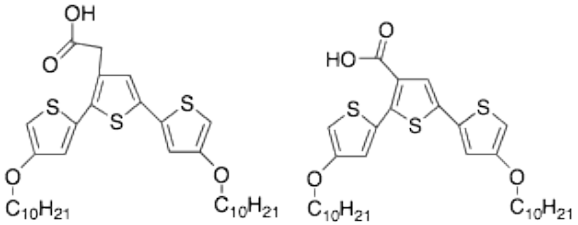
Dante Alighieri, Inferno, Canto XXVI, 118-120.

Outline

- ☑ Introduction
- ☑ p-BSP2 Polymer: Synthesis and Properties
- ☑ Surface Properties
- ☑ AFM Cantilever Functionalisation
- ☑ p-BSP2 - FN interaction: Photochemical Control
- Conclusion and Remarks

INTRODUCTION

TTh & FN



AcTTh **CbTTh**

1876
PHOTOCHROMISM first reported by FRITSCHE

1950
Fischer and Hirshberg studies on SPIRODERIVATIVES

1968
Flannery Jr. TRANSIENT study

1973
Studies on PHOTOCOLOURATION

1974
Surface Proteins role described

1976
FN First evidences for role played in Cancer

1978
McDiarmid, Shirakawa and Heeger synthesised the first CONDUCTING POLYMER

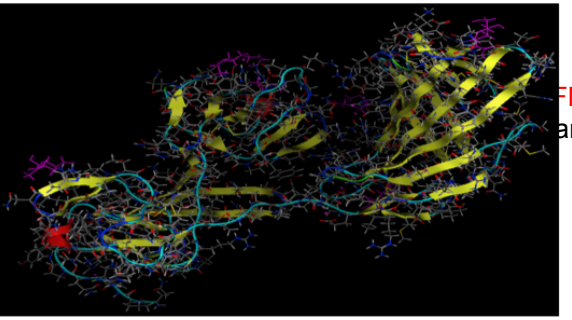
1981
FN Wound Healing role described

1992-1997
Roncali's reviews on p-TTh SYNTHESIS strategies and electronic properties

2000-2010
FN Cell Proliferation studies for anti cancer therapy and Tissue Regeneration

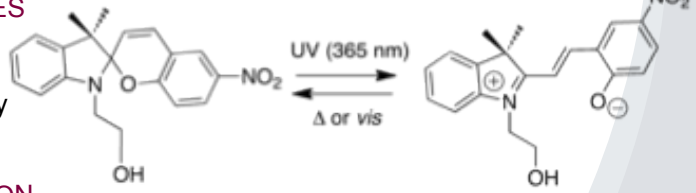
2000-2005
Officer et al. studied new substituted p-TTh

2008-2011
study of Conducting Polymers as platforms for tissue regeneration

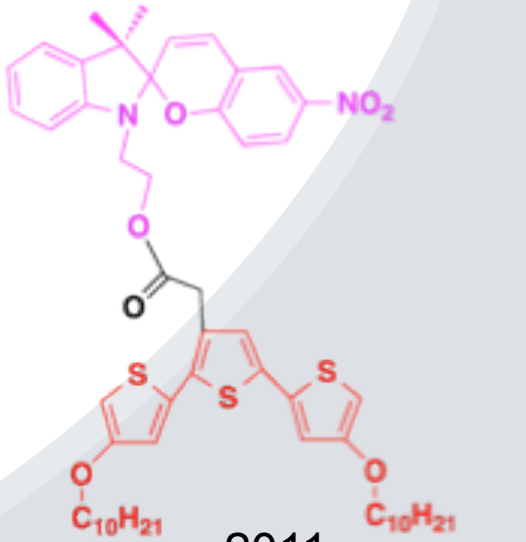


FN

BSP



1997-1999
Goerner studies on RING OPENING mechanism and ligand activity



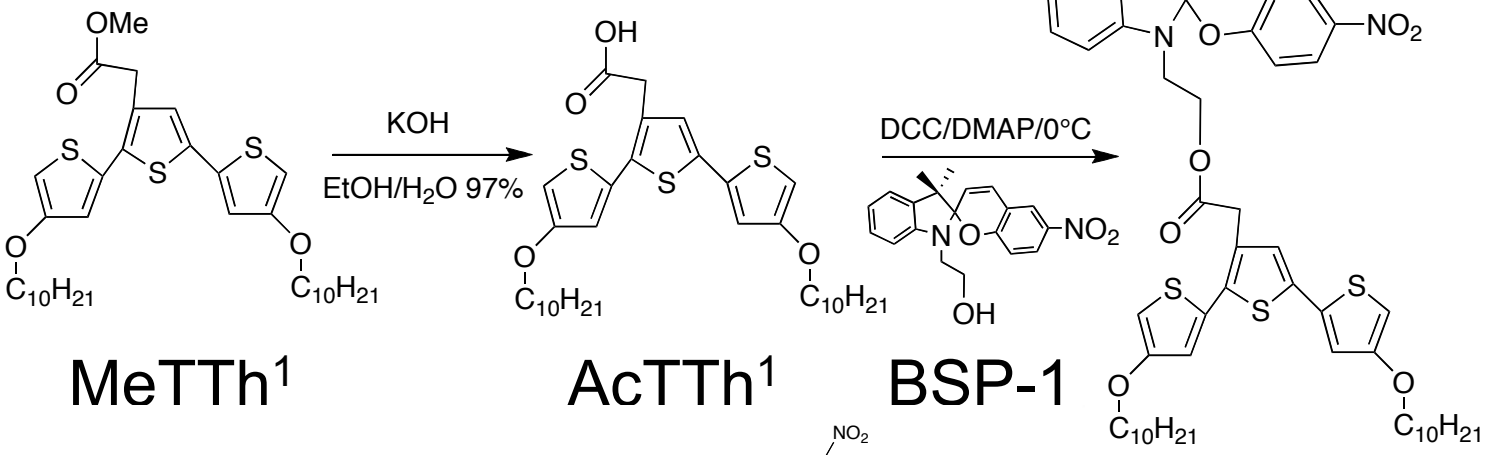
2005-2010
Functionalisation of BSP on Polymeric Surfaces

2011

2012??

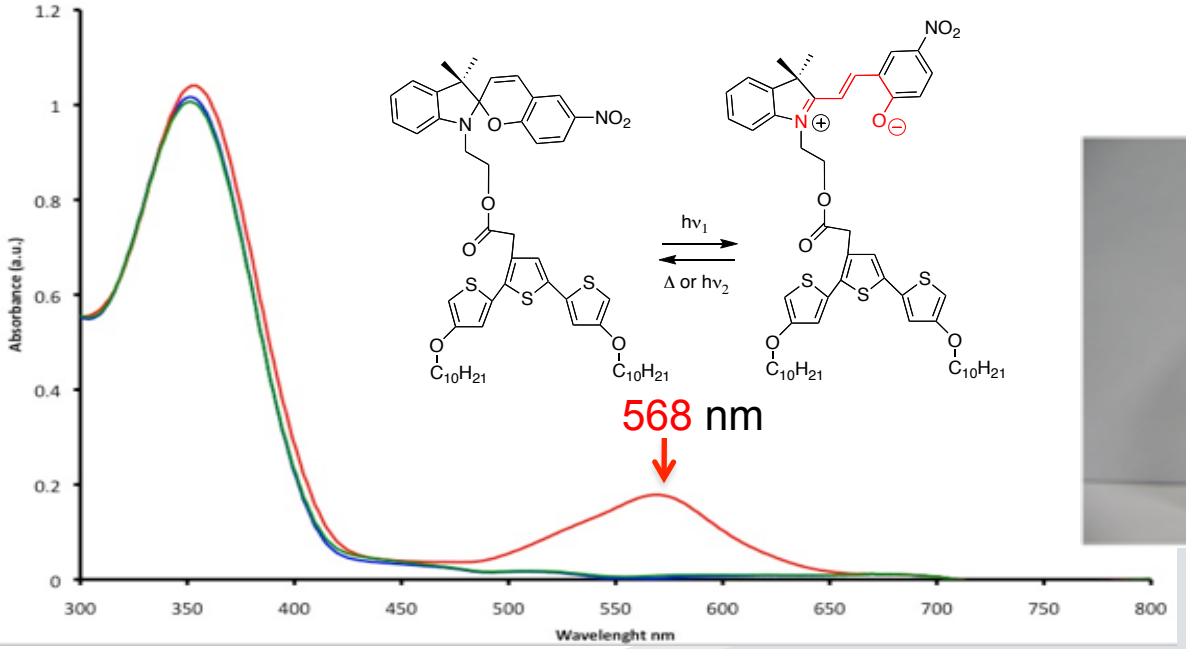
2011
first synthesis of a BSP-TTh based DUAL CONTROL molecule (published on JACS!!!!)

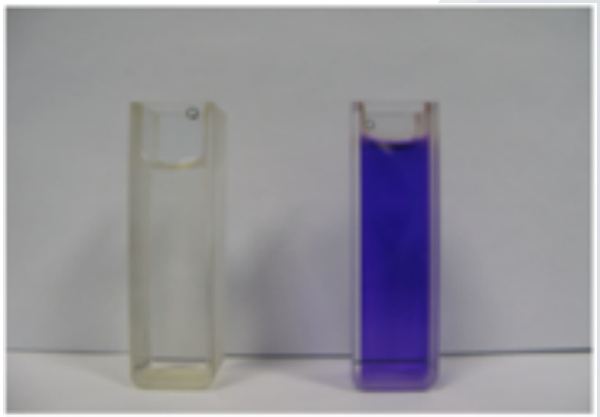
SYNTHESIS of BSP-2



MeTTh[1] AcTTh[1] BSP-1

BSP-2[2]



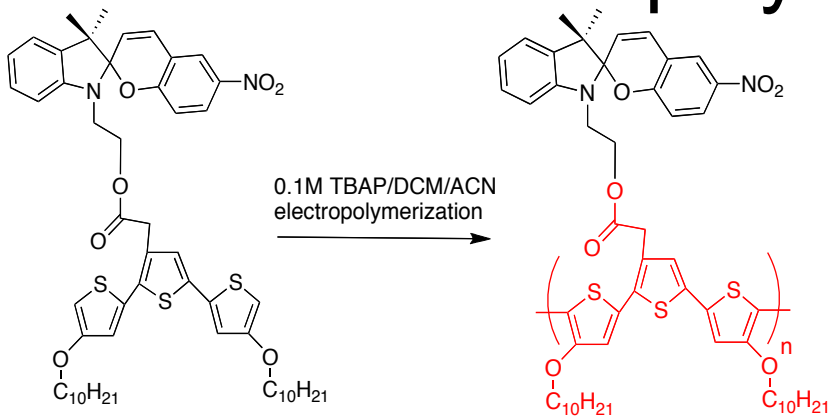


BSP-2 MC-2

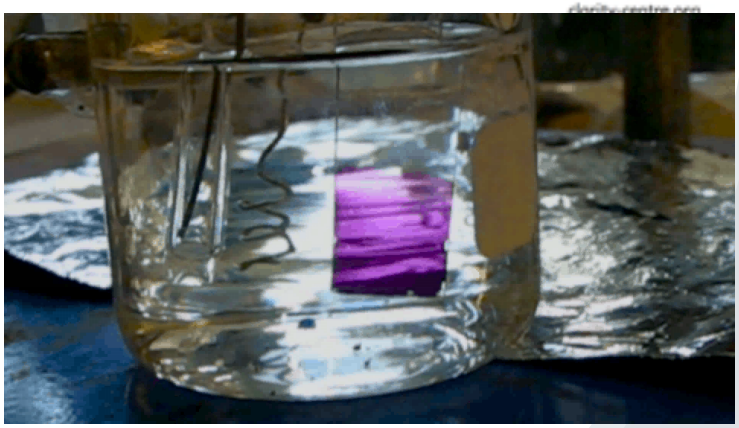
[1] Gambhir, S.; Wagner, K.; Officer, D. L. Synth. Met. 2005, 154, 117–120.

[2] K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G.G. Wallace, and D.L. Officer, J. Am. Chem. Soc., 2011, 133 (14), pp 5453–5462

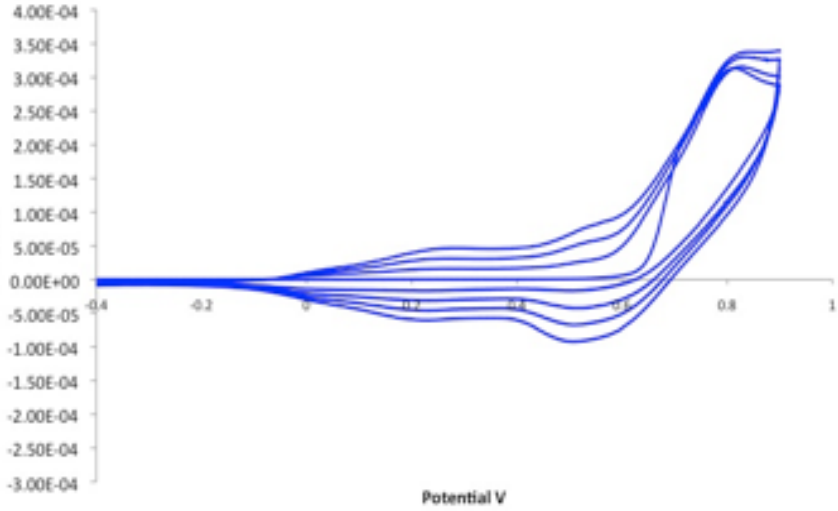
Electropolymerisation



Monomer Concentration	8mM solution of monomer in DCM+ACN, 2:3
Electrolyte	0.1M solution of TBAP buffer in DCM +ACN, 2:3
Working electrode	ITO, PET-ITO
Counter electrode	Pt wire
Reference electrode	Ag/AgCl with $AgNO_3$ 10mM non aqueous.
Scan range	Cyclic deposition From -0.4V to 0.9V
Sensitivity	0.05V per sec
Sweep segments	8



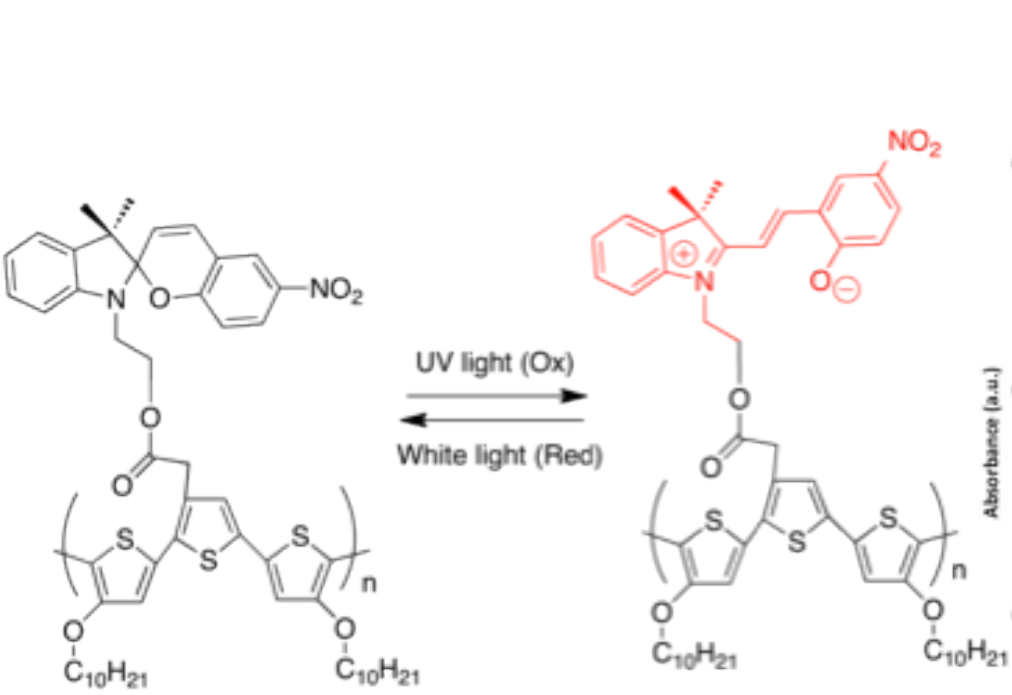
Cyclic deposition of p-BSP2 on ITO



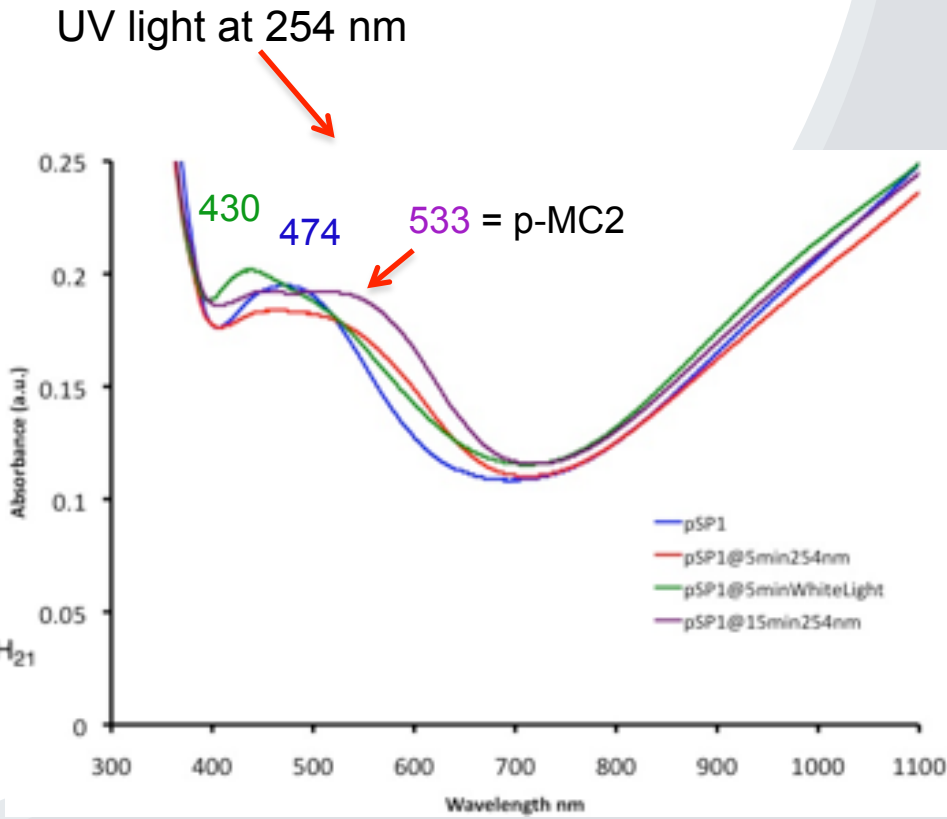
K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G.G. Wallace, and D.L. Officer, J. Am. Chem. Soc., 2011, 133 (14), pp 5453–5462

Photochemical reversibility of p-BSP2

Exposition of p-BSP2 to different cycles of UV-light at 254nm and White light outside the electrolyte.



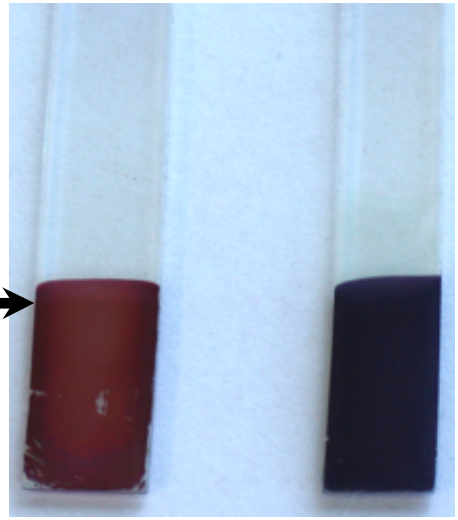
p-BSP2 p-MC2



K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G.G. Wallace, and D.L. Officer, J. Am. Chem. Soc., 2011, 133 (14), pp 5453–5462

Reversibility of pBSP2 ⟷ pMC2: analysis with CONTACT ANGLE

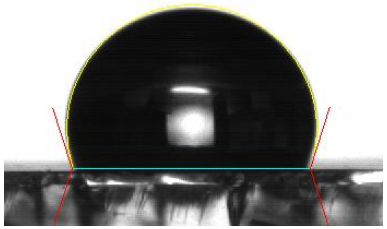
ELECTROCHEMICAL



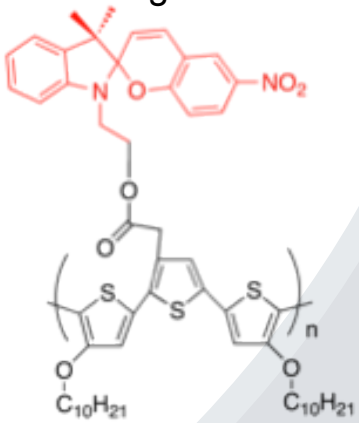
p-BSP2 reduced at -0.4V

p-BSP2 oxidized at 0.8V

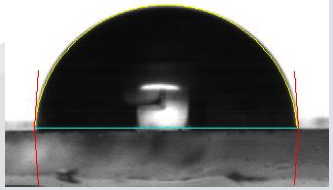
Angle = 107.85 degrees
Base Width = 3.3615mm



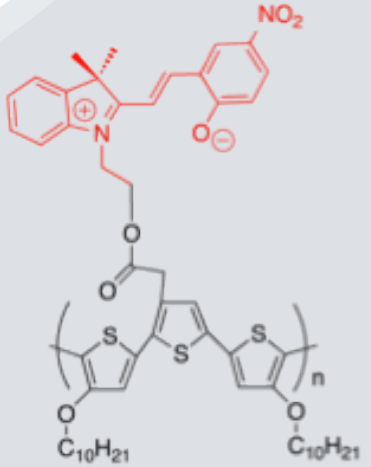
p-BSP2 reduced at -0.4V.
Contact Angle=107.85deg



Angle = 86.47 degrees
Base Width = 4.1982mm



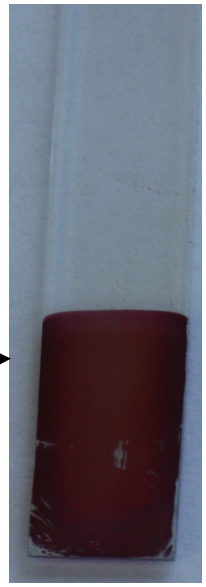
p-MC2 oxidized at 0.8V: contact angle=86.47deg



SYNTHESIS and PROPERTIES

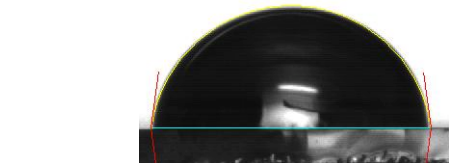
Reversibility of pBSP2 ⟷ pMC2: analysis with CONTACT ANGLE

PHOTOCHEMICAL

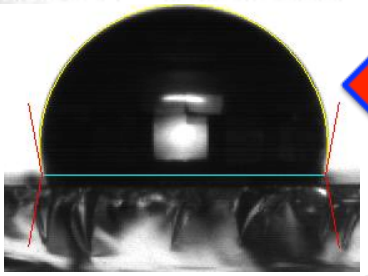


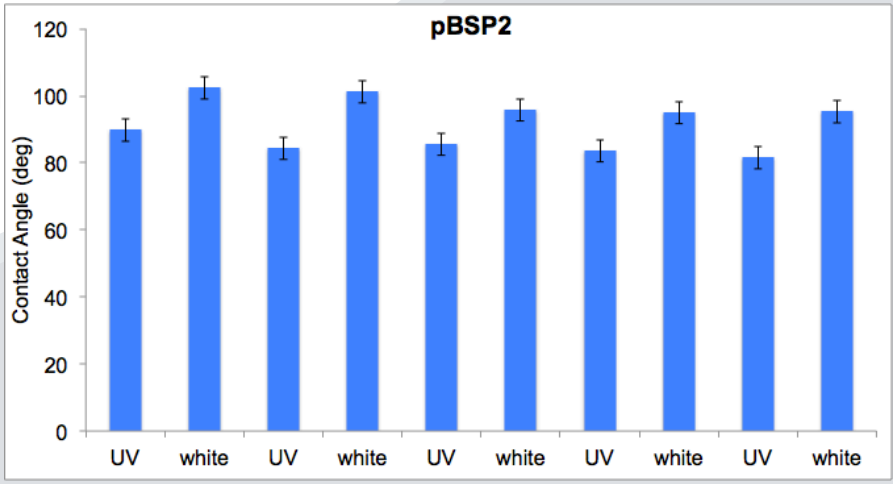
p-BSP2 reduced at -0.4V

Exposure to 254nm UV light for 10minutes



Exposure to white light for 10minutes

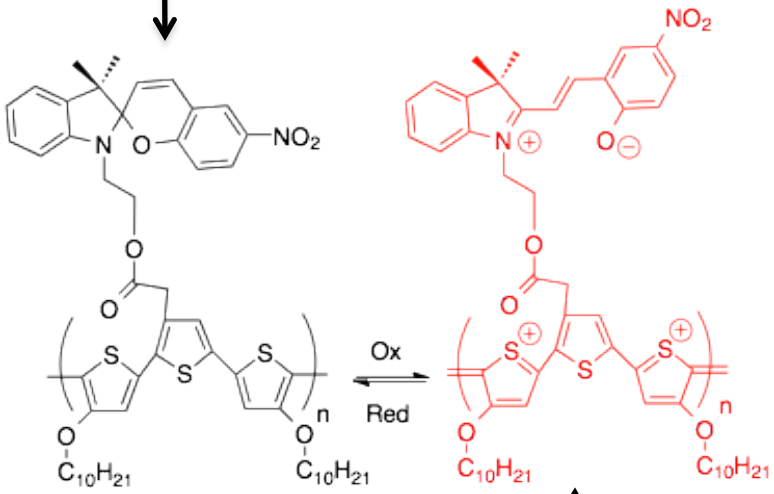




SYNTHESIS and PROPERTIES

AFM and SEM measurements

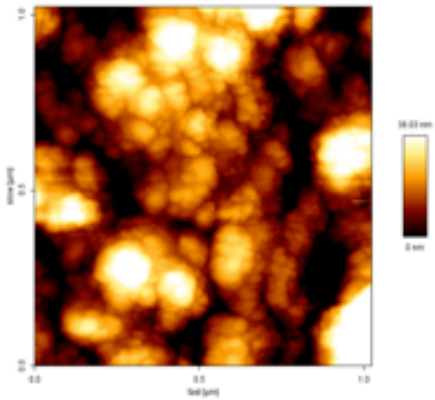
pBSP2 at reduced state



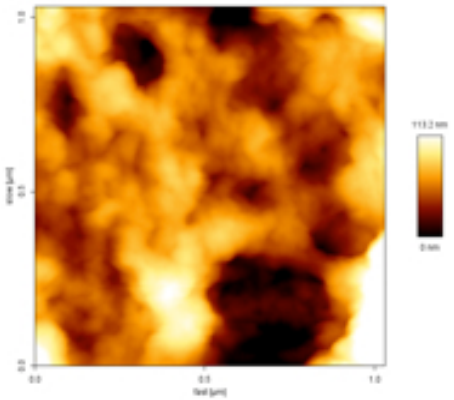
pBSP2 at oxidised state

AFM

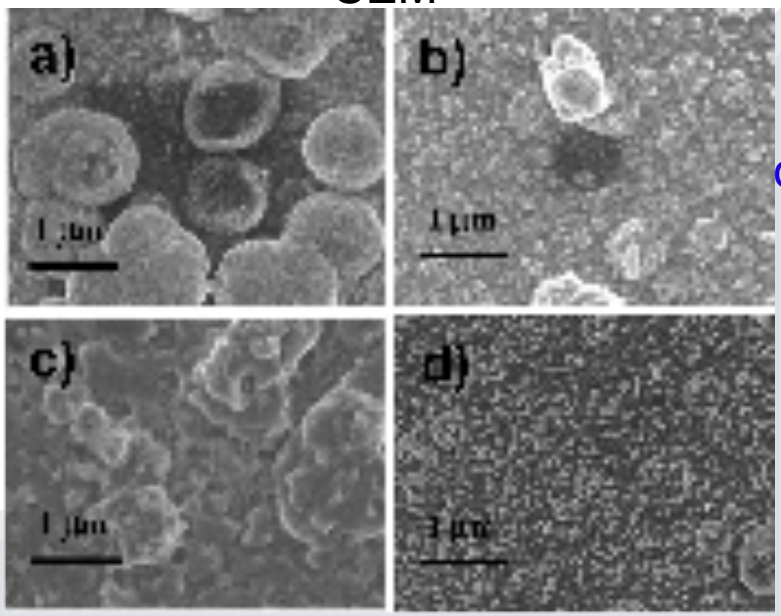
oxidised



reduced



SEM

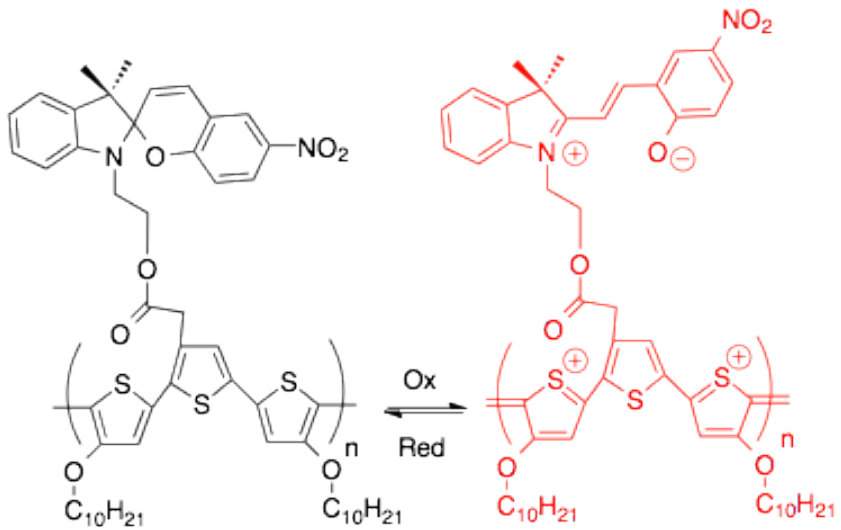


oxidised

reduced

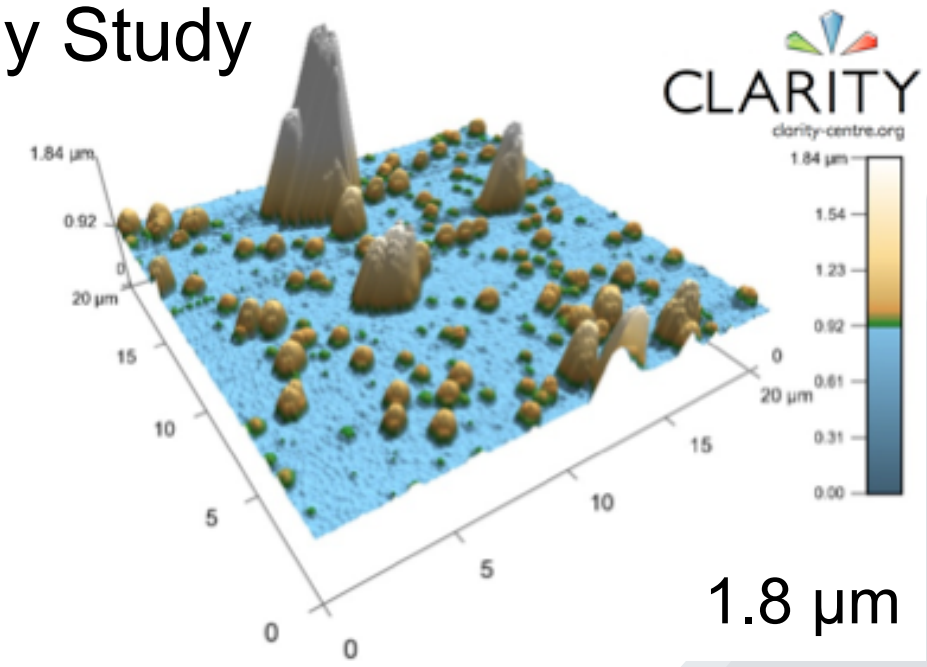
SURFACE PROPERTIES

AFM Morphology Study

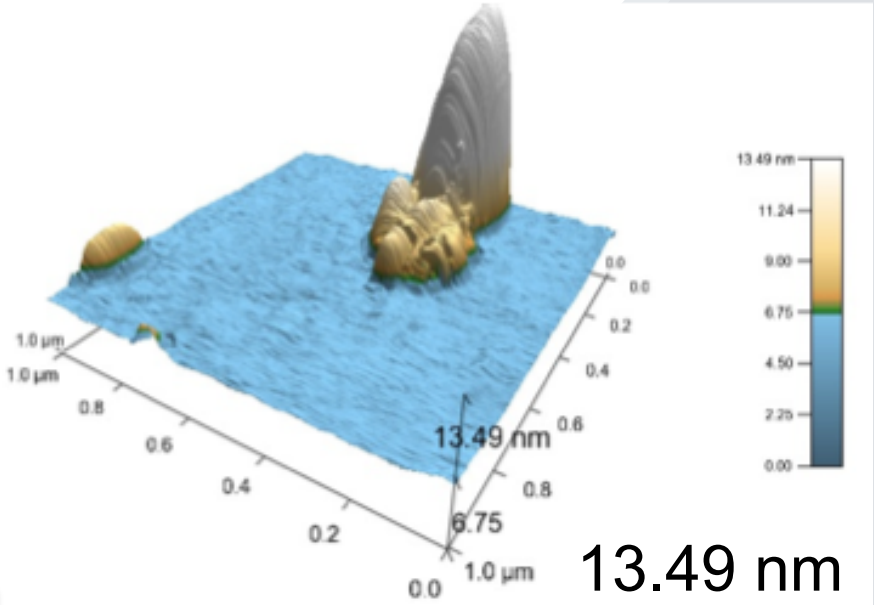


pBSP2 at reduced state

pBSP2 at oxidised state



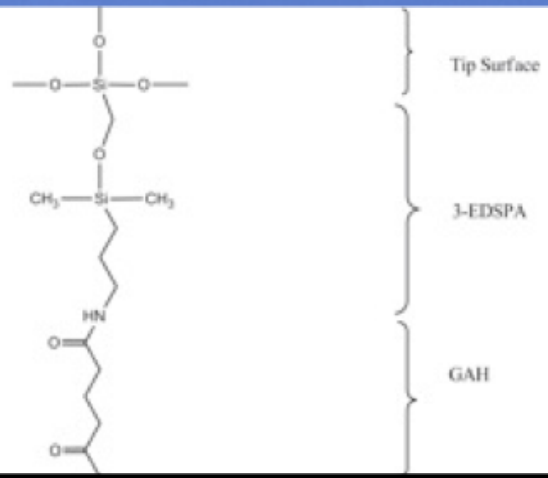
1.8 µm

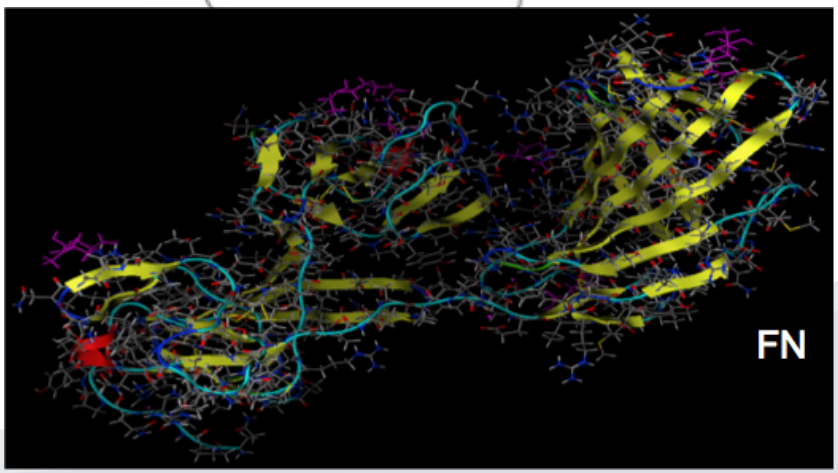


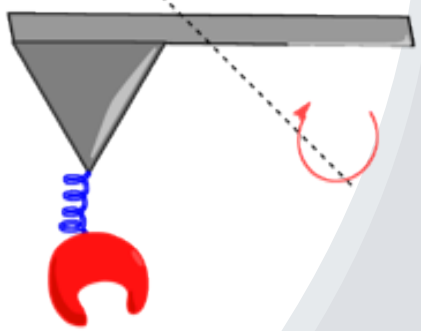
13.49 nm

SURFACE PROPERTIES

AFM Cantilever Functionalisation with FN





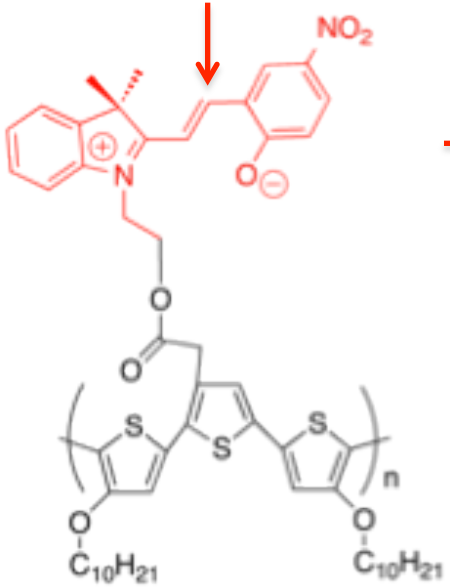


- Gold reflective Nanoworld tips
- Cleaned in plasma cleaner for 5 minutes
- 2 hours in 1% 3-EDSPA solution (in Toluene), then rinsed with toluene and PBS
- 1 hour in GAH solution in PBS and rinsed with PBS
- 1 hour in 10 mg/ml of FN in PBS and rinsed with PBS.
- Stored in PBS in fridge till immediately prior the usage
- Fluorescence spectrum to prove presence of FN
- Calibration

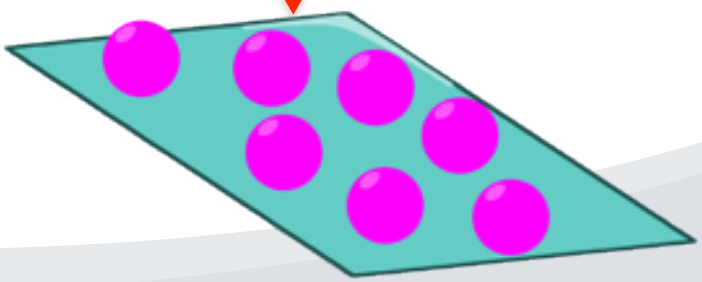
AFM Cantilever FUNCTIONALISATION

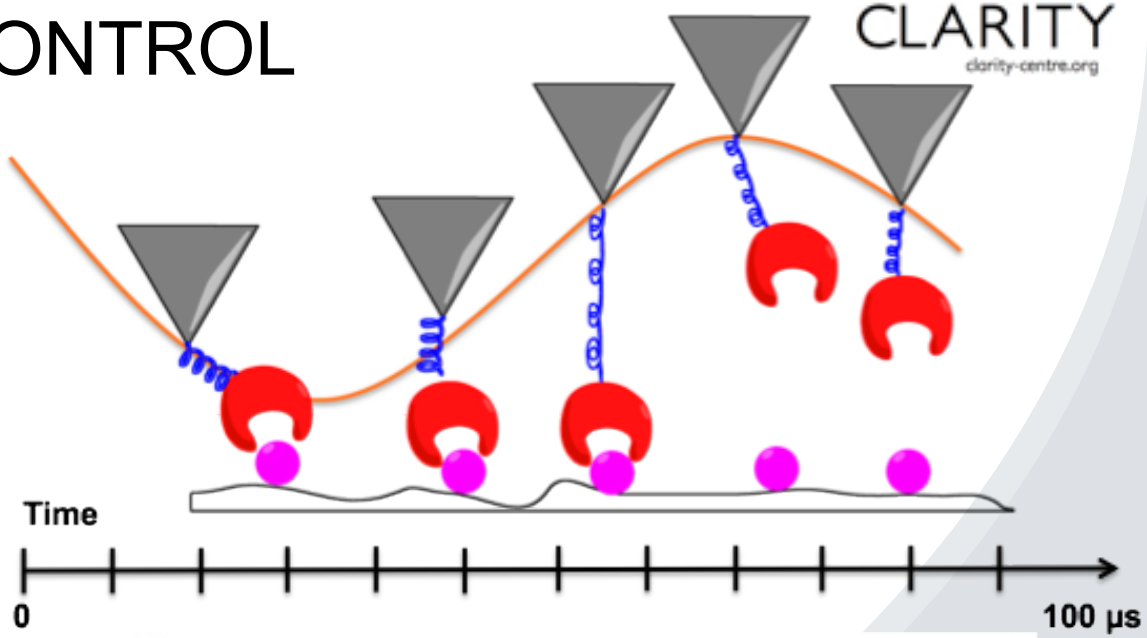
p-BSP2 and FN Interaction: PHOTOCHEMICAL CONTROL

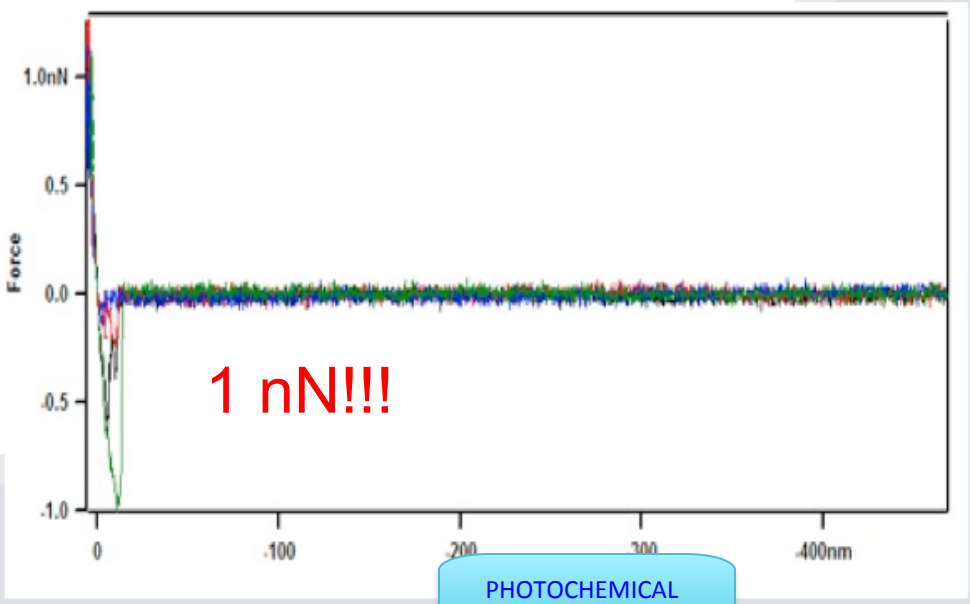
Exposure to 254nm UV light for 10minutes prior the AFM detection



p-MC2 induced



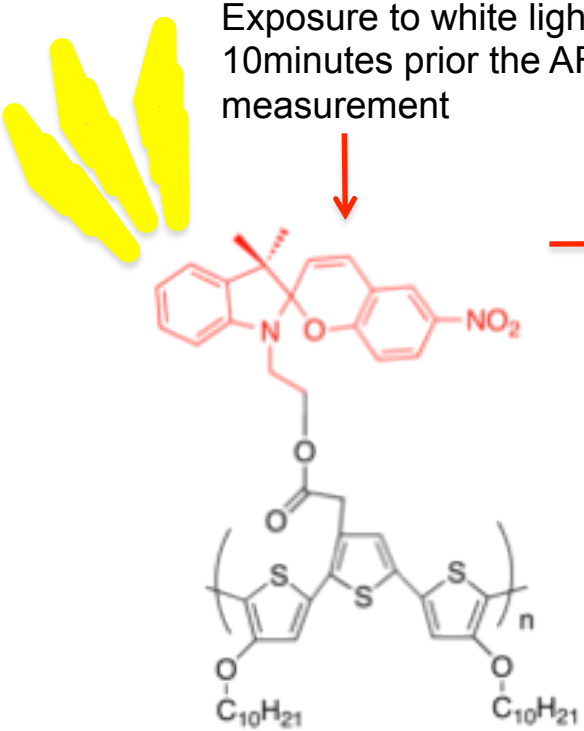




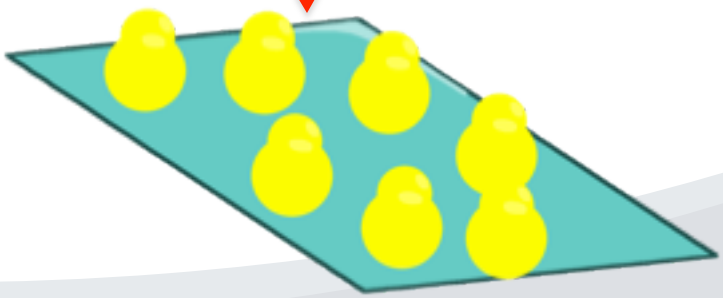
PHOTOCHEMICAL CONTROL

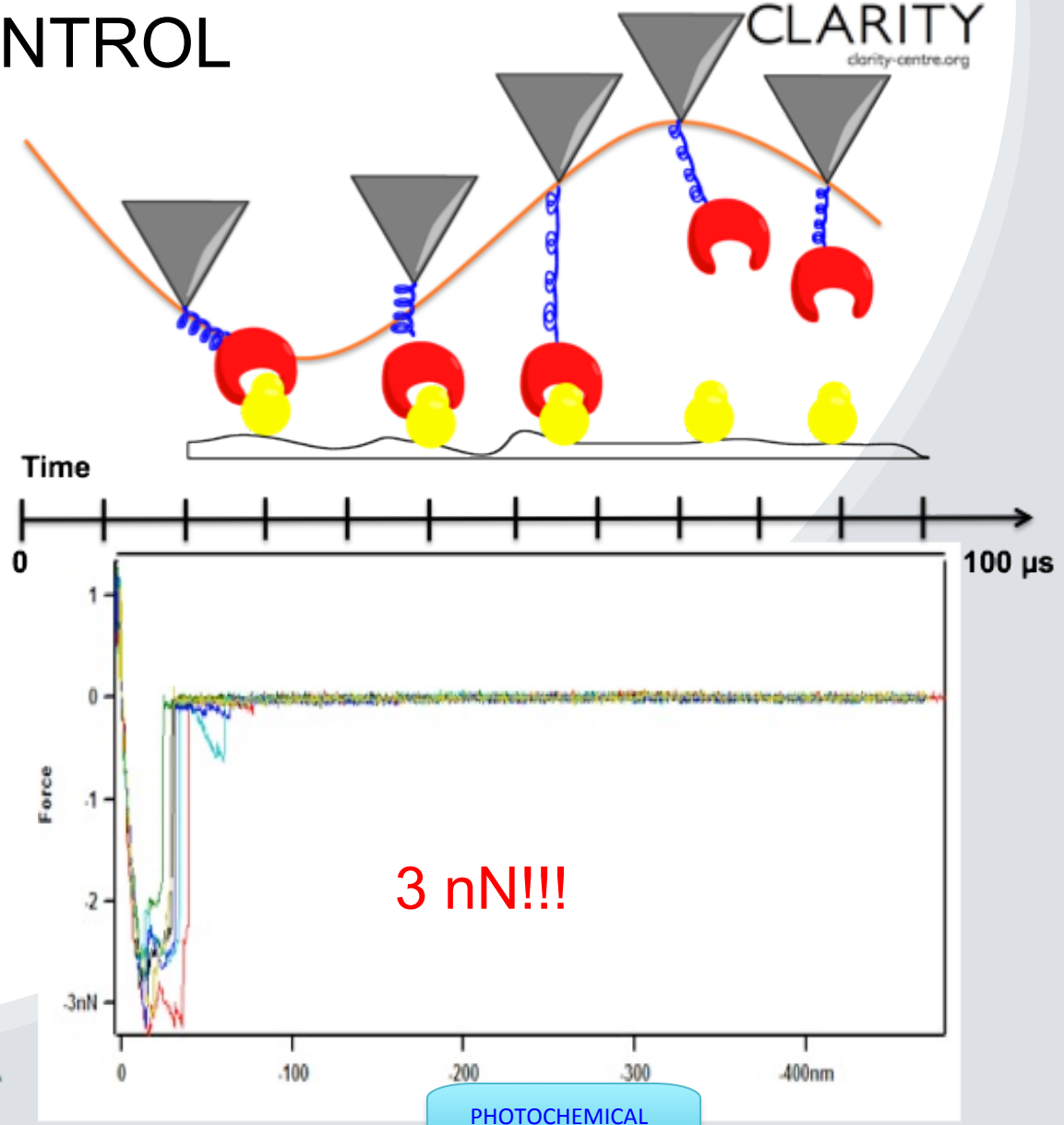
p-BSP2 and FN Interaction: PHOTOCHEMICAL CONTROL

Exposure to white light for 10minutes prior the AFM measurement



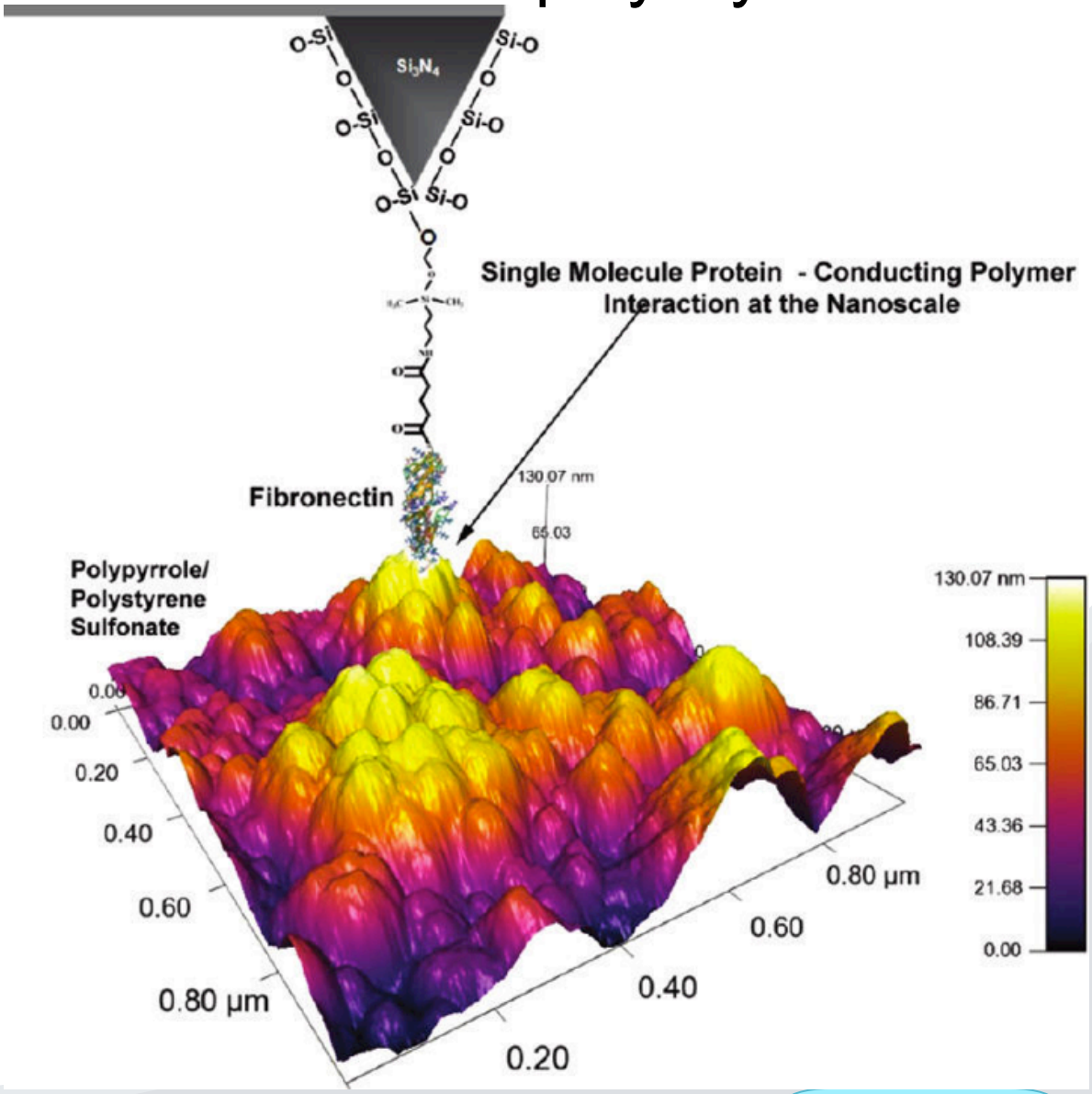
p-BSP2 induced





PHOTOCHEMICAL CONTROL

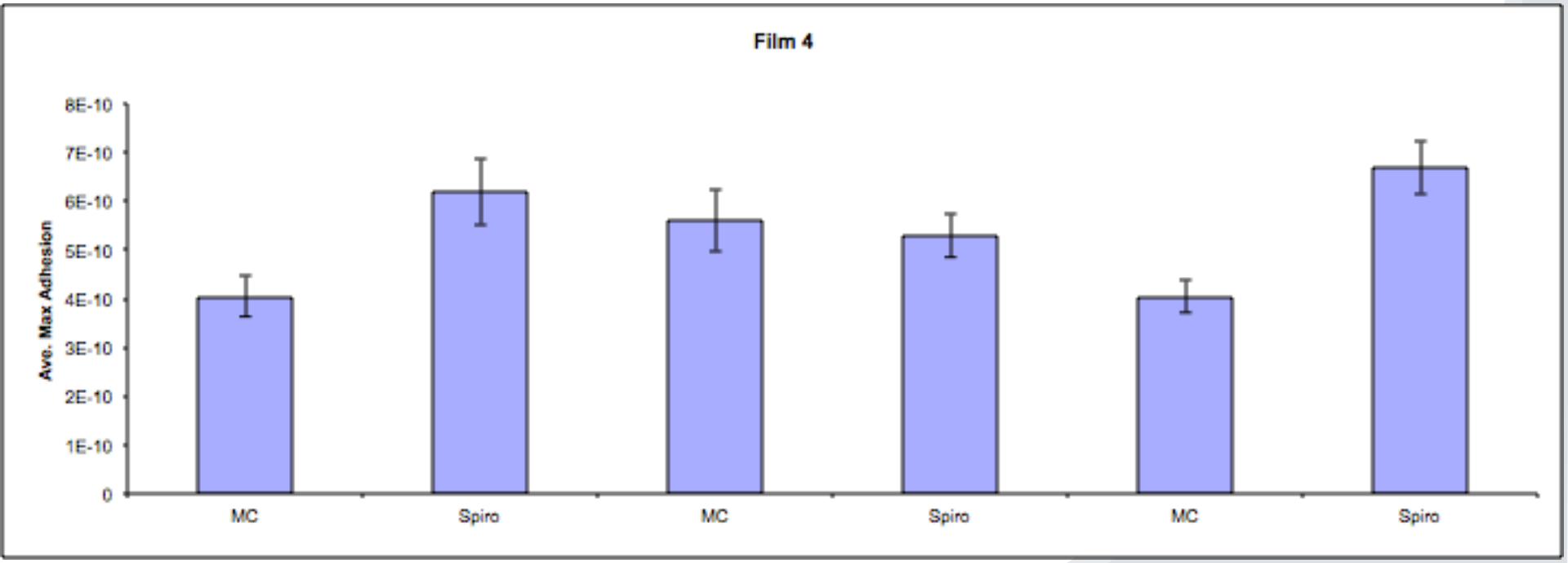
FN Interaction with poly-Pyrrole



M. Higgins *et al.,* Chem. Mater. 2012, 24, 828-839

PHOTOCHEMICAL CONTROL

p-BSP2 and FN Interaction: PHOTOCHEMICAL CONTROL



	Average Max Adhesion	Std Error
p-BSP2	9.56E-10	6.91E-11
p-MC2	7.73E-10	4.02E-11

PHOTOCHEMICAL CONTROL

CONCLUSIONS

- ☑ A new Class of Dual-Control Stimuli Responsive Materials has been Synthesised and Characterised
- ☑ Photo - Electrochromic Properties Have Been Studied
- ☑ p-BSP2 Presents Photo-Actuation and Photo-Reversibility
- p-BSP2 is Able to Generate Lipophilic Interactions with a Fundamental Protein: FN
- The Process is Reversible and Repeatable Over Time

CONCLUSION

Special Thanks to:

- Prof. Dermot Diamond and Dr. Robert Byrne (DCU).
- Prof. Gordon G.Wallace and Prof. David L. Officer (IPRI)
- Dr. Klaudia Wagner, Dr. Michael Higgins and Mrs. Amy Gelmi(IPRI).
- Dr. Kevin J. Fraser, Dr. Fernando Benito-Lopez (DCU).

AND YOU ALL FOR YOUR ATTENTION


Questions???